pecially needed for the discussion of the coacervations explained before.

At any rate, we believe that we have given some enlightenments on the theory of anisotropic colloidal solutions. Some of the origins of analogous phenomena in soap solutions, in disk-shaped tungstic acid sols, or in some lipide systems may be put in the category of our theory. With respect to the role of attractive and repulsive forces in the stability of lyophobic sols and the effect of added salts, the reader should refer to the recent work of Verwey and Overbeek.[5]

[5] E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the stability of Lyophobic Colloids* (Elsevier Publishing Company, Inc., New York, 1948).

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The Infrared Spectra of *N*-Acetylglycine and Diketopiperazine in Polarized Radiation at 25° and at −185°C*

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The infrared absorption spectra of single crystals of N-acetylglycine and of diketopiperazine have been observed at room temperature, and at −185°C, using polarized radiation. The spectrum of the former substance shows some remarkable changes with temperature. In both cases cooling produces a pronounced narrowing of the broad bands due to the vibration of hydrogen atoms involved in strong hydrogen bonds. The two spectra furnish examples of NH absorption in the two extremes of weak and very strong hydrogen bonding. In diketopiperazine two possible interpretations of the doublet structure in the NH valence band are offered.

INTRODUCTION

THE present paper describes the results of an investigation of the polarized infrared spectra of two crystalline substances related to glycine, N-acetylglycine and diketopiperazine (glycine anhydride). The crystal structures of both these substances have been determined by x-ray methods and are of a particularly simple type. In view of this comparative simplicity it was felt that a study of the infrared spectra of these substances might provide worthwhile information of the relationship between spectrum and structure in amino acids and related compounds.

CRYSTAL STRUCTURES[1,2]

The crystals of both acetylglycine and diketopiperazine are monoclinic and belong to the space group C_{2h}^5. In Fig. 1 we have shown a unit cell diagram for acetylglycine. In Fig. 2 two views of the unit cell of diketopiperazine are shown. For the first substance the essentially planar molecules (exclusive of the hydrogen atoms) lie parallel to (100). The molecules are presumably joined together by a two-dimensional network of hydrogen bonds, as indicated in the figure. For the second substance, the planar molecules (again exclusive of the hydrogen atoms) lie almost parallel to (101). The inclination of the molecular planes to this crystallographic plane is approximately 6°. The molecules are joined together by the system of hydrogen bonds as shown in the figure.

It is worth pointing out the germane features of the hydrogen bonds. In acetylglycine a bond is formed between two oxygen atoms of different molecules. The O—H···O distance is 2.56 au, which is one of the shortest bonding distances of this type so far reported. On the other hand the bond formed between a nitrogen of one molecule and an oxygen of another is rather long

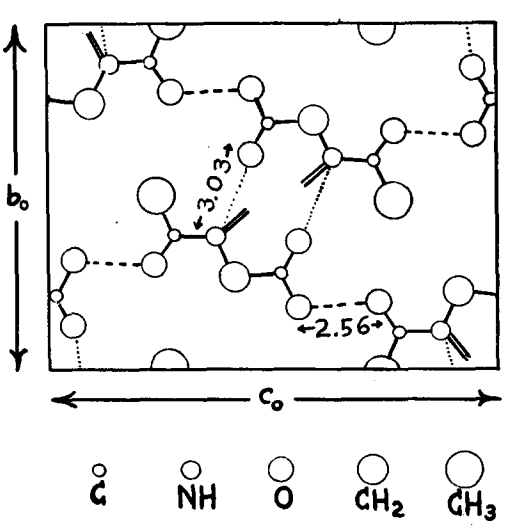

FIG. 1. Unit cell of N-acetylglycine. A view perpendicular to (100). The dashed and dotted lines show the hydrogen bonds. The doubled lines represent the spectroscopically determined directions of the N—H bonds (after Carpenter and Donohue).

* This investigation was supported by the ONR under contract N6-ori-102, VI.
† Contribution No. 1558.
[1] G. B. Carpenter and J. Donohue, J. Am. Chem. Soc. **72**, 2315 (1950).
[2] R. B. Corey, J. Am. Chem. Soc. **60**, 1598 (1938).

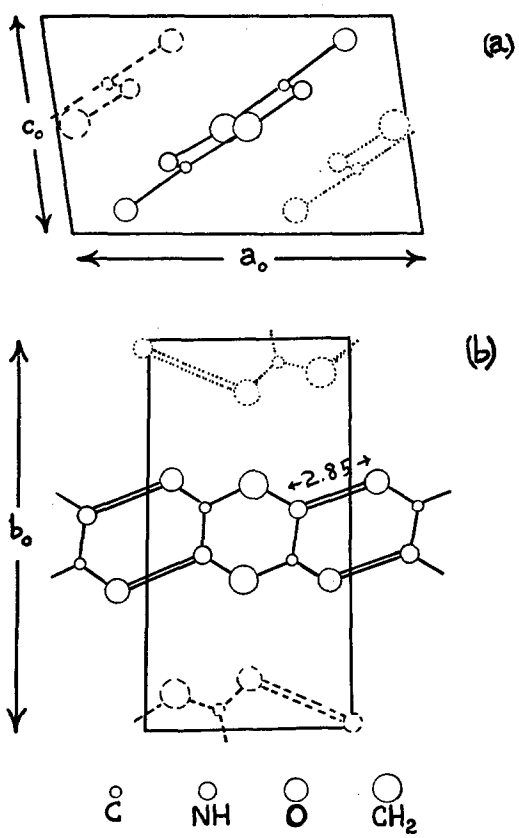

FIG. 2. Unit cell of diketopiperazine (a) View perpendicular to (010). (b) View perpendicular to (101). The doubled lines show the hydrogen bonds (after Corey).

for an N—H···O bond, 3.03 au. In diketopiperazine the N—H···O bonds are in contrast quite short, 2.85 au. These bond lengths and the accompanying implications of bond strengths will be important in our subsequent discussion of the spectra.

SELECTION OF ORIENTATIONS

As was pointed out elsewhere[3] the selection of orientations for the observation of polarized spectra in crystals of the monoclinic system may be a difficult task. Fortunately for the crystals studied in the present work the relative simplicity of the crystal structures considerably reduced this job. In the crystals of both substances the heavy atoms of a given molecule have been shown to be very nearly coplanar. The median planes of all molecules are parallel, and indeed parallel to the **b** axis. To an approximation quite adequate for our purposes we may regard the molecules as having a plane of symmetry, and the normal modes as divided into two classes which are symmetric and antisymmetric with respect to reflection in this plane. Consequently whatever transient electric moment is generated by a given vibration will either be parallel or perpendicular to the symmetry plane. Generalizing to the crystal, it is therefore readily seen that to obtain maximum information, observations should be made with the electric vector of the light beam either parallel to or perpendicular to the parallel symmetry planes, i.e., to the median planes of the molecular skeletons.

For the observation of the in-plane motions a further simplification is possible since the **b** axis lies, in both cases, in the plane paralleling the molecules. Observations of motions in this plane should be made with the electric vector of the light beam parallel or perpendicular to **b**, since the latter is a symmetry-fixed eigenvector of the complex dielectric tensor.

The foregoing arguments of course have meaning only in the case of a plane parallel light beam incident upon the crystal. In the present work this is not the situation. The micro-illuminator used produces a convergent beam incident upon the sample. This in turn has the effect of introducing into the observed spectrum contributions from an unwanted source. That is, one must expect to find the spectrum, which is characteristic for the electric vector vibrating perpendicular to the face of the crystal section being studied, superimposed upon the spectrum of interest. Data are not available for making an accurate calculation of this mixing but an estimate based on very simple considerations indicated that in our apparatus the observed spectrum would consist of about 80 to 90 percent of the desired component. This degree of purity is adequate for qualitative considerations.

EXPERIMENTAL

A. Apparatus

The spectra were taken both with a Beckman IR-2 spectrometer (NaCl optics) and in the region from 4000 to 2800 cm^{-1} with a vacuum grating instrument.[4] The samples, whose preparation is described subsequently were mounted at the focus of an all reflecting infrared microscope or micro-illuminator having an evacuable housing and provided with means for cooling the sample

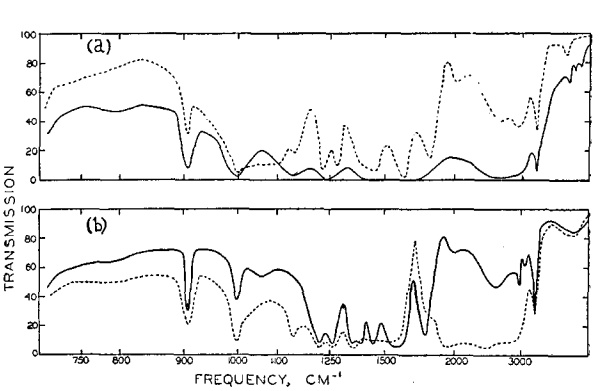

FIG. 3. Spectra of N-acetylglycine at 25°C. (a) Spectra of (011) section about 30μ thick. Solid curve for $E\|(100)$, dashed for $E\perp$intersection (100) and (011). (b) Spectra of (100) section about 5 to 10μ thick. Solid curve $E\|\mathbf{b}$, dashed $E\|\mathbf{c}$.

[3] R. Newman and R. S. Halford, J. Chem. Phys. **18**, 1276 (1950).

[4] Badger, Zumwalt, and Giguère, Rev. Sci. Instr. **19**, 861 (1948).

holder to liquid air temperature. Polarization was produced by means of a silver chloride polarizer.[5,6]

Our micro-illuminator will be described elsewhere in detail, but a few remarks regarding the construction and operation of the low temperature equipment may be of interest. As in other cells for low temperature work recently described,[7,8] the sample holder projects from the inner thimble of a Dewar vessel, which, in our instrument, extends as a side arm from the casing of the micro-illuminator. The stainless steel Dewar tube is attached with a sylphon bellows, and adjusting screws are provided so that the sample under observation can readily be adjusted in the optical focus without breaking the vacuum.

Using an oil diffusion pump with suitable water-cooled baffle an operating pressure of about 2×10^{-5} mm was obtainable. Even at this pressure, the rate of ice formation on the cooled sample was not negligible. However, spectra could be taken for somewhat over an hour after the initial cooling before an ice band ($\sim3\mu$) of objectionable intensity developed, which, allowed sufficient time for our work. Presumably, if the various gasketed joints were made more permanent than was convenient for us to do, both the operating pressure and the related rate of ice formation would have been considerably reduced. The thermal efficiency of the system is comparatively high. The initial cooling consumed about 50 ml of liquid nitrogen and the subsequent rate of consumption was about 40 ml per hour. The sample reached thermal equilibrium at about -185°C in about 5 minutes after the initial introduction of refrigerant. The temperature was measured on a trial run by imbedding a chromel-alumel thermocouple in a sheet of silver chloride placed in the position normally occupied by the sample.

TABLE I. Frequencies (cm^{-1}) observed for acetylglycine.[a]

b_0		c_0	⊥(100)	Intensity	Tentative assignments
4500		4500		w	2×OH stretch
3340	=	3340		s	N−H stretch
3150				w	2×1600
2980				w	C−H stretch
2500		3000			OH stretch
	≪	to		vs	2×1280
2000		1850			2×1000
1750	>	~1750		s	C=O stretch (carboxyl)
1600	>	1600			C=O stretch (acetyl)
		to		vs	
1440	>(?)	1400			CH_2, CH_3 bends
1350	<	1350		s	NH_2 bend, CH_2 wagging, twisting
1280	<	1280		s	
1220	<	1220		s	CH_3 bends
		1150		w	
1060				w	
			~1020	w	
1000	<	1000		s	C−N−C stretch
905	<	905		s	
770		770		w	

[a] The inequalities give the relative intensity in the two orthogonal directions b and c. The symbol ~ indicates a shoulder. Since our data for the third column were obtained from a crystal section which produced a mixing of the three spectra (b, c, ⊥(100)) we have elected to omit in the third column any frequency which appears in the first two. This would be in accord with the theoretical mutual exclusion of the (100) and ⊥(100) spectra.

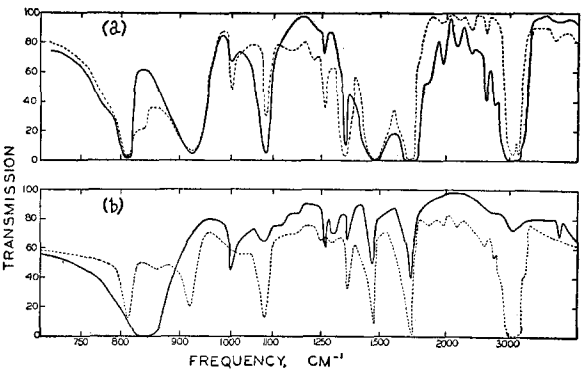

FIG. 4. Spectra of diketopiperazine at 25°C. (a) Spectra of (101) section about 20μ thick. Solid curve $E\|[101]$, dashed $E\|\mathbf{b}$. (b) Spectra of (010) section about 10μ thick. Solid curve $E\perp[101]$, dashed $E\|[101]$.

B. Preparation of Samples

Acetylglycine

Small crystals (several millimeters on an edge) of this substance were grown from aqueous solution at room temperature. For these crystals and for those of diketopiperazine, identification was achieved by reference to their well-described optical, geometrical, and mechanical properties.[1,2] Sections with faces parallel to (100) were obtained by cleaving the crystals parallel to this plane with a razor blade. Sections about 60μ thick could be obtained in this way. These were further thinned by a hand-polishing technique essentially like that previously described.[3] The final product was a section somewhat less than 10μ thick. Some attempts were made to prepare sections using a microtome. The results were not, however, as satisfactory as those of the aforementioned method, although some usable specimens were obtained.

After the sections were prepared they were mounted on a mask of thin copper sheet. As the crystals did not always completely cover the hole in the mask, additional masking was obtained by means of pieces of aluminum foil cemented to the copper sheet. The mask was then attached to a brass strip which could in turn be mounted on a modified goniometer head. The latter allowed the crystal to be carefully placed at the focus of the micro-illuminator. This mounting procedure was employed for all the specimens used.

As was pointed out previously we would have liked to obtain a section of acetylglycine whose faces were perpendicular to the molecular plane (100). However, because of the marked cleavage of the crystals parallel to this latter plane, this ambition was not fulfilled. Sections which were approaching a suitable thickness would invariably fracture and be rendered useless in some stage of the procedure. As an alternative, although not a

[5] R. Newman and R. S. Halford, Rev. Sci. Instr. **19**, 270 (1948).
[6] N. Wright, J. Opt. Soc. Am. **38**, 69 (1948).
[7] E. L. Wagner and D. F. Hornig, J. Chem. Phys. **18**, 296 (1950).
[8] A. Walsh and J. B. Willis, J. Chem. Phys. **18**, 552 (1950).

TABLE II. Frequencies (cm^{-1}) observed for **b** spectrum of acetylglycine at 25° and −185°.[a]

25°	−185°	25°	−185°
3340	3340		1170*
3150	3150	~1150	
2980	2980		1130*
2930	2930		1095*
2500	2500		1065*
	2280*	1060	
	2020*		1005*
2000		1000	
~1950	~1950		995*
1820	1820	905	910
1750	1750		
1600 to 1500	1600 to 1500		
1440	1440		
1400			
1380	1380		
1300 to 1220	1320* 1280* 1230*		
	1205*		

[a] The symbol ~ indicates a shoulder. The starred frequencies are those which are manifest only at the low temperature. This table refers to spectra taken from a sample about twice as thick as that to which the spectra of Table I belong. Consequently certain weak bands are listed here which do not appear in that table.

completely satisfactory one, it was found possible to prepare sections with faces parallel to (011). This plane makes an angle of about 45° with (100). Although the same difficulty was encountered as before, by occasional good fortune a usable specimen was obtained.

Diketopiperazine

Crystals of this substance were grown from aqueous solution at 50°C. At this temperature fairly large thin plates formed whose faces were parallel to (010). By further polishing of these plates suitable specimens about 10μ thick were produced. From other more symmetrically formed crystals, sections with faces parallel to (101) were obtained. For this purpose, due to the poor solubility of this substance, a slight departure from the conventional technique was employed. The innovation was simply the use of a microtome to plane the crystals down parallel to (101). In the final thinning operation the hand-polishing technique was again employed. Sections about 20μ thick were obtained in this way.

RESULTS AND DISCUSSION

The spectra of acetylglycine at room temperature are shown in Fig. 3, those of diketopiperazine in Fig. 4. A listing of the observed frequencies, their intensity-orientation relationships and assignments are given in Tables I, II and III. In these tables a number of bands are given several alternative assignments or none at all. The frequencies and polarization data provided insufficient information to allow for unambiguous assignments in these cases.

No particular purpose would be served by discussing the complete spectra in detail. Both the molecules and their spectra are too complex for such a treatment. However, it does seem worth while to study those features of the spectra which are not overwhelmingly complex or obscure and which perhaps can yield additional information concerning the crystal structures and dynamics. The discussion which follows points out what we believe to be the more important results in this connection.

A. Acetylglycine

Two strong hydrogen stretching fundamentals would be expected to appear in the spectrum of this substance, one due to the N−H bond and the other to the O−H bond.[9] For reasons that will become apparent from the subsequent discussion we ascribe the sharp band at 3340 cm^{-1} to the N−H stretching vibration and the broad intense band extending from 1850 to 3000 cm^{-1} to the O−H stretching. The relatively weak C−H stretching band appears at 2980 cm^{-1}.

The band at 3340 (N−H) is of only moderate intensity and is quite narrow, (half-width approximately 40 cm^{-1}). A study of the polarization behavior of the band for several samples seemed to indicate that the change in electric moment of the individual molecule projected in the (100) plane is directed at 45±10° to the **c** axis.‡ For reasons given it was not possible to obtain data that would conclusively demonstrate that the component in a direction perpendicular to the (100) plane is zero. However, structural considerations would indicate that in all probability the N−H bond is very nearly parallel to this plane, a conclusion supported by our limited data. We can consequently infer that the angle between the N−H bond and the bond joining the nitrogen and central carbon atom is approximately 100°. The error in this estimate may be as large as 10°, but is not so large as to admit the possibility that the hydrogen atom lies on a line connecting nitrogen and oxygen atoms, (i.e., the dotted lines of Fig. 1) which requires an angle of 132°.

All these observations strongly support the conclusion that the N−H···O hydrogen bond is very weak, as was indicated by the long N−O distance of 3.03A. The sharpness of the band indicates very weak coupling of the N−H vibration with lattice modes as contrasted with the O−H vibration to be discussed. The position of the hydrogen atom relative to the oxygen is rather unfavorable for the formation of a strong hydrogen bond and the H−N−C angle is roughly that to be expected in the absence of any hydrogen bond. The observed angle is 100°±10°, whereas in the isolated molecule it

[9] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 195.

‡ This angle was obtained by the usual Lambert's law calculation on the band center. The I_0 used was taken to be the mean of the transmission values on the apparent edges of the band.

might be expected to lie between the limits 109° and 120°.

The frequency of the N−H band is of considerable interest since if the relation between frequency shift and strength of hydrogen bond can be quantitatively understood, it should be of great assistance in elucidating the structure of crystalline polypeptides and proteins. This frequency in acetylglycine differs by only about 10 cm^{-1} from that found in some fibrous proteins[10,11] and in some synthetic polypeptides[12] where, furthermore, the bands are also relatively sharp. However, on the basis of these facts one would probably not be quite justified at this time in asserting that the N−H···O bonds in these substances are as weak as in acetylglycine, since the N−H frequency is dependent on other factors not as yet completely understood.

The absorption region extending from about 1850 to 3000 cm^{-1} is very remarkable both for its great breadth and for its high intensity. We are not aware that any band quite similar to it has previously been reported. For reasons discussed subsequently we ascribe it to the OH valence vibration with frequency greatly shifted by the extremely strong hydrogen bonding, and greatly broadened as a consequence of the unusually strong coupling with lattice vibrations.

The band is strongly polarized and appears with maximum intensity when the electric vector is parallel to the **c** axis of the crystal. Of all the hydrogen valence vibrations this behavior is to be expected only in the case of the O−H vibration, as one may see by reference to Fig. 1. From considerations regarding bond angles and the extremely short O−O distance of 2.56A, it seems highly probable that the hydrogen atom lies at least very nearly on the line connecting the two oxygen atoms which it links. Changes in dipole moment arising from its vibration should consequently be very nearly parallel to the **c** axis.

The band is extremely broad and its mean frequency is extremely low for an O−H vibration. This is undoubtedly a consequence of the strong hydrogen bonding and possibly might have been anticipated by an extrapolation of the observations on the lower fatty acids. The acetic acid dimer, for example, in which the O−H···O distance is 2.76A,[13] exhibits an absorption extending over about 1200 cm^{-1} with a maximum shifted about 600 cm^{-1} from the normal frequency of unbounded OH.[14]

As a check on the above interpretation we have made observations on KH_2PO_4 in which an O−H···O distance of 2.54A has been shown to exist.[15] In a single crystal of this substance we found a broad, intense absorption covering essentially the same region as in acetylglycine. The polarization behavior was consistent with its assignment to an O−H valence vibration. While the character of the O−H···O bonds cannot be expected to be entirely equivalent in the two compounds, nevertheless they are probably sufficiently similar so that the comparison of the two spectra is valid.

In the hope of throwing further light on the nature of the broad O−H absorption an investigation of the low temperature spectrum was undertaken. In Fig. 5 the **b** spectra of a single crystal taken at both room temperature and −185°C are shown. A number of rather surprising differences between the two spectra is exhibited.

First, there would appear to be a slight decrease in the intensity of the 3340 N−H band. Next, it would appear that there is some decrease in the intensity of the residual O−H band, particularly on the high frequency side. This is perhaps indicative of a narrowing of the band as the temperature is lowered (see subsequent discussion for diketopiperazine). The apparent narrowing of several other bands and accompanying general increases in transmission throughout the spectrum are also to be noted.

A number of apparently new bands make their appearance in the low temperature spectrum. These

TABLE III. Frequencies (cm^{-1}) observed for diketopiperazine.[a]

b_0		[101]		⊥ b_0 and [101] (out of plane)	Intensity	Tentative assignments
		~3450			w	
3280	<	3300 to 2940	≫	3000	vs	N−H stretch +2×1700, 3×1070
		2800			w	2×1470, 2×1070+810
		2750			w	
2550	<	2550			w	2×1340, 1340+1260, 2×915+810
2300	>	2300			w	1340+1000, 3×810
2130	<	2130			w	2×1070
2000	<	2000			w	2×1000
~1800	<	~1800			w	2×915, 1000+815
1720 to 1660	<	1740 to 1640	>	1710	vs	C=O stretch
~1520		~1520			w	
1490 to 1450	<	1490 to 1450	>	1470	vs	CH_2 scissors
1340	>	1340	>	1340	s	N−H in plane bend[b]
		~1290	<	1290	w	
1260	>	1260		1260	w	
1220	>	~1220			w	
1180				~1180	w	Ring stretchings, CH_2 bendings except for 840 which is an out of plane bending, probably of C=O
				~1150	w	
1070	<	1070	>	1070	s	
1000	>	1000		1000	w	
915		915			vs	
~840			<	840	vs	
810	<	810			s	
~780					w	

[a] The inequalities signs give the relative intensities in the three mutually orthogonal directions. The symbol ~ indicates a shoulder.
[b] Suggested by deuteration experiments.

[10] Ambrose, Elliott, and Temple, Nature **163**, 859 (1949).
[11] M. Goldstein and R. S. Halford, J. Am. Chem. Soc. **71**, 3584 (1949).
[12] E. S. Ambrose and A. Elliott, Proc. Roy. Soc. (London) **A205**, 47 (1951).
[13] J. Karle and L. O. Brockway, J. Am. Chem. Soc. **66**, 574 (1944).
[14] Buswell, Rodebush, and Roy, J. Am. Chem. Soc. **60**, 2239 (1938).
[15] J. West, Z. Krist. **74**, 306 (1930).

either have no counterpart in the room temperature spectrum or at best appear there in a very weak and diffuse form. Particularly surprising is the presence of two fairly intense bands at 2020 and 2280 cm^{-1}. Strong absorption is usually not to be expected in this region for substances of the type being investigated here. The set of new frequencies are listed in Table II.

It was first thought that these new absorptions were spurious and resulted from the condensation of water vapor, carbon dioxide, or even diffusion pump oil on the cooled samples. However, unlike the behavior of condensation bands the intensity of these new absorptions in the acetylglycine spectrum were constant over a period of more than an hour and a half. Furthermore, a blank specimen of AgCl produced no trace of such bands when subjected to the normal cooling procedure. Not even after two and a half hours had passed after the initial cooling and the ice band at 3μ had become quite intense was there any evidence for these absorptions. The spectra of other crystals (e.g., diketopiperazine, glycine) that have been examined under comparable conditions likewise gave no evidence of these bands. It would therefore seem that the new low temperature bands are indeed real.

In some cases, notably in the 1250 cm^{-1} region and perhaps the 1000 cm^{-1} band, it appears as if the low temperature bands were better resolved versions of the room temperature band envelopes. In these instances the explanation may lie in the sort of band narrowing that has been observed in the case of diketopiperazine (see Sec. B).

It is a little difficult to understand the possible origin of some of the other bands. The fact that the single crystals survive cooling and reheating seems to rule against a first-order transition at some intervening temperature which would in any pronounced way alter the crystal structure. However, it is possible that some minor modification (e.g., "freezing in" of the motions of the methyl groups, small changes in lattice dimensions) could produce rather large changes in the intensity pattern. In the absence of further information, however, it would not seem profitable to prolong the discussion at this time.

B. Diketopiperazine

In the region from 3300 to 2940 cm^{-1} we have observed a band of extreme intensity, and breadth of around 300 cm^{-1} at half-height. In those views of the crystal for which the absorption is not overwhelmingly intense the band is resolved into two components. The major of these appears at 3000 cm^{-1} and its somewhat less intense companion at 3280 cm^{-1}. This apparent doubling of the band has been observed before.[16–18] Both components appear to exhibit the same polarization behavior. Several much weaker bands observed only as shoulders are also found. The intensity of the lower frequency component and the frequency of its companion seem to preclude the possibility that the band is due in any large part to the C—H stretching vibration. (The 2980 C—H band of acetylglycine serves as a suitable comparison.) We therefore feel quite confident that at least the greatest contribution to this band must come from the N—H stretching vibration, a view which is in accord with its polarization behavior. In the (010) view of the crystal the N—H absorption should be almost entirely confined to the orientation in which the electric vector is parallel to [101]. For the (101) view of the crystal the intensity ($E||[101]$) should be greater than the intensity ($E||b$). These expectations are borne out by the data.

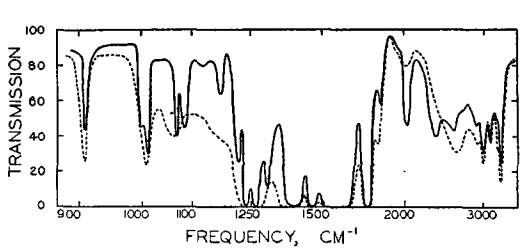

FIG. 5. Spectra of N-acetylglycine for $E||b$ at 25°C (dashed curve) and −185°C (solid curve). Sample about 10 to 15μ thick.

The presence of structure in the region of N—H absorption has previously been observed in several cases. It has been the subject of considerable discussion and has been variously interpreted. In the case under discussion it is reasonable to attribute the major component of the band to the one active N—H valence vibration. For its companion two reasonable explanations are suggested.

The individual molecules of diketopiperazine have centers of symmetry in the crystal. This should be expected to result in an exclusion rule which in first approximation prohibits the appearance of the overtones and combinations of even parity derived solely from infrared active fundamentals. However, the possibility of combination of active and inactive fundamentals is in no way restricted. Indeed in the region 2000–3000 cm^{-1} a number of weak bands appear which can be comfortably attributed to combinations of an active and an inactive fundamental, wherein the inactive frequencies are assumed to be virtually identical with the active ones. This assumption seems completely reasonable and could presumably be verified by a Raman spectrum. If the foregoing arguments are valid then from the observational viewpoint there is no selection rule and any combination band could be expected.

For the 3280 cm^{-1} band we have chosen two such combinations as being most probable. The first possibility is that the band is derived from the combination of the active and inactive C=O frequencies.

The second possibility is the assignment of 3280 cm^{-1} to the third overtone of 1070 cm^{-1}. The latter we ascribe

[16] Buswell, Downing, and Rodebush, J. Am. Chem. Soc. **62**, 2759 (1940).
[17] H. Lenormant, Ann. Chim. **5**, 459 (1950).
[18] L. Kellner, Proc. Roy Soc. (London) **A177**, 447 (1941).

to a ring vibration involving chiefly the C—N bonds having partially double bond character. Since this vibration might be expected to interact strongly with the N—H stretching vibration a resonance of 3×1070 cm^{-1} with the NH band could give intensity to the former. The 1070 cm^{-1} band is presumably a fundamental because of its rather high intensity. It is rather unlikely that it is a hydrogen bending fundamental since only the CH_2 wagging vibration would have the correct polarization behavior, and in other molecules the frequency of this mode is considerably higher. Furthermore, the intensity is rather too great. The assignment of 1070 cm^{-1} to the ring vibration mentioned seems reasonable both on the basis of frequency and regarding the presumed interaction with the N—H valence vibration. From observations on other molecules it is evident that the N—H linkage is very sensitive to the character of the bonding of the nitrogen atom to other atoms.

The band at 1470 presents some problems. It has the frequency to be expected for a CH_2 scissors vibration but has, in part, the wrong polarization behavior and also a rather high intensity. These effects are perhaps due in part to an overlay of some other bands (the corresponding region in glycine, for example, shows fine structure) and in part to some interaction with the C=O vibration.

The effect on the N—H band of cooling the sample to −185°C is particularly marked. In Fig. 6 two sets of spectra taken under different conditions of polarization are shown. The second set (Fig. 6(b)) is perhaps the more striking. It is seen that the lower frequency component seems to shrink more or less symmetrically about its band center as the sample is cooled from 25° to −185°. Such band narrowing, when observed, is usually attributed to a decrease in the anharmonic coupling between molecular modes and lattice modes, as the population numbers of the higher states of the latter decrease with temperature. More simply, the classical amplitude of the lattice oscillations decreases with temperature producing a smaller broadening. That the effect is so marked in the present case is perhaps best explained by the existence of large interactions between the N—H molecular mode and the lattice through the mechanism of the strong N—H···O bond. In the opposite sense the breadth of the N—H band at room temperature is of course attributed to the strong hydrogen bond.

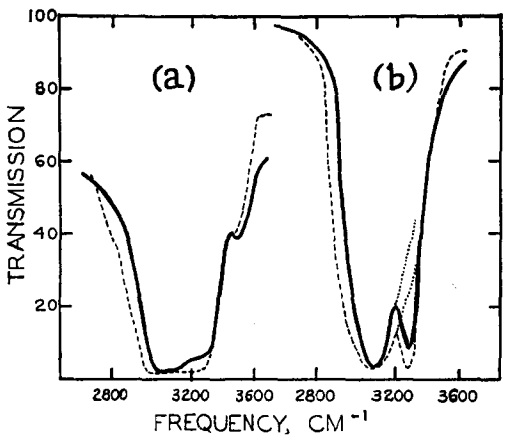

FIG. 6. N—H band of diketopiperazine at 25°C (dashed curve) and −185°C (solid curve). (a) $E\|[101]$. (b) $E\|b$.

The higher frequency component seems to show decreased intensity on cooling. However, it would seem that this effect results more from the position of this band as a satellite to the other more intense band than to any intrinsic modification in the former. The dotted lines in Fig. 6(b), representing the probable course of the spectral curves in the absence of the satellite, point out the basis for our view.

The two spectra of Fig. 4**b** (the (010) view) would presumably be mutually exclusive if the molecular planes accurately lay in the (101) plane and if observations had been made in parallel light. A certain amount of overlapping is observed, however, more than can be accounted for by the slight tipping (6°) of the molecular planes out of (101). This is perhaps in large part due to our use of strongly convergent light to whose disadvantages we have referred before.

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